



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C01G 23/053, C01B 39/00, B01J 23/00	A1	(11) International Publication Number: WO 99/43616 (43) International Publication Date: 2 September 1999 (02.09.99)
(21) International Application Number: PCT/IL98/00090 (22) International Filing Date: 24 February 1998 (24.02.98) (71) Applicant (for all designated States except US): ROTEM AMFERT NEGEV LTD. [IL/IL]; P.O Box 15292, 77051 Ashdod (IL). (72) Inventors; and (75) Inventors/Applicants (for US only): MIRSKY, Yaacov, W. [IL/IL]; Ben Yehuda Street 13/5, 84363 Beer Sheva (IL). GORLOVA, Marina, N. [RU/RU]; Prospect Pobedy, 9, Kirishi, 187110 (RU). (74) Agent: LAVIE, Simon; P.O. Box 6202, 31060 Haifa (IL).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, US, UZ, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: A MODIFIED TITANIUM DIOXIDE AND A METHOD FOR ITS PREPARATION (57) Abstract <p>The present invention relates to a titanium dioxide composition modified with urea in the stage of the titanium hydroxide precipitation from an aqueous solution. The aqueous solution, contains a mixture of dissolved sulfate salts, including titanyl sulfate, following a hydrothermal treatment of the precipitated titanium hydroxide in its mother liquor. The modification of said titanium dioxide is carried out with a basic silica sol in the stage of the formed titanium hydroxide or dried titanium dioxide. The titanium dioxide composition is characterized by an enhanced thermal and hydrothermal stability of the pore structure, a developed mesopore structure, a decreased sulfur content and a specific surface area formed by pores with a diameter up to 490 m²g⁻¹ for a calcined material at a temperature of 800 °C for 3 hours.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

A MODIFIED TITANIUM DIOXIDE AND A METHOD FOR ITS PREPARATION

The present invention relates to Titanium dioxide. More particularly, the invention relates to a novel modified Titanium dioxide and method for its preparation.

BACKGROUND OF THE INVENTION.

Titanium dioxide has been known to be produced by drying or calcining of Titanium hydroxide. There are various methods of producing Titanium hydroxide from different types of Titanium compounds.

Three crystalline forms of Titanium dioxide are known in the art: Anatase, Rutile and Brookite. Anatase or amorphous Titanium dioxide partially crystallized into Anatase, are commonly used as catalysts (for example see US Patent No. 4,388,288 and US Pat. No.4,422,958).

In most catalytic processes carried out in gas phase or liquid phase it is extremely viable to use catalysts with developed meso and macropore structure, which accounts for a high catalytic activity and for a high rate of reagents diffusion inside granules or shaped blocks of catalysts, and diffusion of reaction products outside the catalysts structure.

Mesopore structure is determined by the method of the active material precipitation from a solution and its subsequent treatment.

Macropore structure is determined mainly by the process of granulation or shaping.

Many catalytic processes are carried out under increased temperatures where Titanium dioxide undergoes shrinkage. Its active surface area is reduced and its activity is also decreased. Since the heat treatment will take a long period of time, the Titanium dioxide aging process leads to its structure transformation from Anatase to Rutile crystalline form, and these alterations cause a significant decrease in its catalytic activity. Since Titanium dioxide is quite an expensive material it is most desirable that such catalyst should possess a prolonged effective period of use.

In order to increase the thermal stability of Titanium dioxide, various additives were suggested. Thus, in order to increase its stability, when it is obtained from Titanium oxychloride by precipitation with an aqueous solution of ammonia at a pH of 7.8, at least one stabilizing agent is incorporated . Useful agents for this purpose may be selected from aluminium, sodium, potassium, calcium or other chlorides, nitrates and powdery silica. The criterion of thermal stability is based on the change in the specific surface area of a sample calcined at 575 degrees C for seven hours, compared with a sample calcined only for one hour at the same temperature (see French patent application No. 2,621,577 and European Patent Application No. 0311,515).

Several investigations were performed in the field of Titania/Silica mixed oxides preparation. The idea of this approach is a coprecipitation of titanium hydroxide and silicic acid,

Titania/Silica mixed oxides preparation and their use as supports for Nickel catalyst were described (Journal of Catalysis 105, p. 511-520 1987). As mentioned therein, a mixed oxide was precipitated from a mixture of $TiCl_4$ and $SiCl_4$.

Precipitation of titanyl sulfate in the presence of a powdery dry silica (SYLOID- -74) was carried out in order to prepare samples containing 20%, 40% and 80% by weight TiO_2 and investigations with these precipitates as catalyst for selective catalytic reduction of NO_x , were described in: Applied Catalysis A, General 139, 1996 , pages 175-187.

The method for the preparation of Titania-Silica mixed oxides with alkoxide sol-gel method was described in Journal of Catalysis, 153, p.165-176 (1995). As mentioned therein, tetra-isopropoxy-titanium and tetra-methoxysilicon were used as starting materials. Various titania-silica aerogels obtained by an alkoxide-sol-gel route, were prepared and tested in the reaction of epoxidation of olefins (Journal of Catalysis 153, 177-189, 1995),

Crystalline titanium silicates having specific adsorption and catalytic properties were described in literature (Advances in Catalysis, Vol. 41, 253-327, 1996).

The above brief review illustrates the importance attributed to the subject of obtaining a novel type of titanium dioxide.

It is an object of the present invention to provide a novel modified Titanium dioxide and methods for its preparation. It is another object of the present invention to describe various uses of the novel modified Titanium dioxide.

BRIEF DESCRIPTION OF THE INVENTION

A novel titanium dioxide modified with urea in the stage of a titanium hydroxide precipitation from an aqueous solution containing a mixture of dissolved sulfate salts, including titanyl sulfate, following a hydrothermal treatment of the precipitated hydroxide in its mother liquor and then modified with a basic silica sol in the stage of the formed titanium hydroxide or dried titanium dioxide, being characterized by a high catalytic activity, an enhanced thermal stability as measured by a specific surface area of up to 240 m²/g for a sample in which 15% of silicon (calculated as SiO₂) was introduced into the titanium hydroxide structure during the interaction with basic silica sol and calcined at 800°C for three hours. The above novel titanium dioxide composition is most useful as a catalyst in many fields such as photocatalyst and as a carrier in catalyst compositions for removal of organic materials present in air. A method for the preparation of the above modified titanium dioxide is also described.

DETAILED DESCRIPTION OF THE INVENTION

Modified titanium dioxide is prepared from two types of starting materials.

- 5 The first one is an aqueous solution containing a mixture of dissolved sulfate salts including titanium sulfate, having a pH up to 1.7.

The second one is titanium hydroxide or titanium dioxide prepared by any known method.

- 10 In the first case, titanium dioxide is prepared from titanium hydroxide precipitated and hydrothermally treated in its mother liquor in the presence of urea and further modified with basic silica sol.

In the second case, titanium hydroxide or titanium dioxide in the form of dough, paste, or suspension, is brought to a pH in the range of 6.0-11 with urea or ammonia and then interacted with a basic silica sol.

- 15 The first type of starting materials includes solutions of a double salt ammonium titanyl sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$, commercially produced as acid titanyl sulfate solution, for example UNITi 992 or a similar acid titanyl sulfate solution prepared with different titanium dioxides, or titanium hydroxides dissolved in sulfuric acid. In another case, for
20 example the dried titanium hydrolysates commercially produced (UNITi 908TM, FINNTi S-230) can be dissolved in sulfuric acid with a concentration of about 70%, producing an acid titanyl sulfate solution.

- Both commercial acid titanyl sulfate solution and a similar one prepared as described above, have to be partially neutralized to a maximum pH as
25 mentioned above. These partially neutralized solutions contain a mixture of titanyl sulfate with other sulfate salts. Typical examples of these sulfate salts are: sodium sulfate, potassium sulfate, calcium sulfate, magnesium sulfate and ammonium sulfate. These partially neutralized solutions can be used as starting materials for the modified titanium dioxide
30 preparation.

The solution of the above mentioned ammonium titanyl sulfate salt may be used as a starting material in its aqueous solution containing besides titanyl sulfate, ammonium sulfate, the pH of this solution being in the range of 0.7 to 0.9.

- 5 In contrast to the usual commercial titanium dioxides or similar products manufactured by known methods, the modified titanium dioxide produced from the first type of starting materials as mentioned above, is characterized by a specific combination of high surface area, an enhanced thermal and hydrothermal stability of the pore, a crystalline
10 structure, a decreased sulfur content and a high catalytic activity.

Typical examples of the second type of starting materials are the intermediate products of titanium pigment UNITi 902TM and final materials produced by FINNTi S-140TM and FINNTi-150TM.

- 15 Titanium Hydroxide cake precipitated according to the European Patent Application No. EP 0722905 A1 (after washing but without adding potassium hydroxide and phosphoric acid) as well as Titanium Hydroxide or Titanium Dioxide precipitated according to U.S. Patent No. 4,929,586 (before vanadyl oxalate addition) can be also used as a starting material of the second type.

- 20 The thermal stability of modified titanium dioxide produced from the second type of starting material is similar to that of modified titanium dioxides produced on the basis of the first type of starting material. The modified titanium dioxides produced on the basis of the second type of starting materials, are characterized by a decrease in the sulfur content
25 compared with the starting materials.

Titanium dioxide possessing the above improved properties are unknown up to the present invention.

According to the present invention, two modifiers can be used during a particular procedure for producing the novel modified titanium dioxide.

- 30 These modifiers are urea and basic silica sol i.e. a colloidal solution of silica having a pH of above 7.0 .

Urea is a known commercial product, which can be used either in a solid form or in an aqueous solution.

There are known silica sols colloids which contain particles of silica with a diameter in the range of 2-100 nm. The inner part of each particle,
5 consists almost of dehydroxylated silica, while silicon atoms located on the outer part of each particle, are hydroxylated. Silica sols can be stable, if some cations compensate the negative charge of silica particles. Among the useful cations to be present, it should be mentioned sodium, potassium and ammonium. Commercial silica sols, prepared with any
10 known procedure, usually with a cation exchange method, can be used as modifiers.

Such sols can also be prepared during the process of modified titanium dioxide preparation with any other known procedure.

Basic silica sol is used as a modifying agent for the formed titanium
15 hydroxide or for the dry titanium dioxide. The titanium hydroxide is separated from the mother liquor and washed. The titanium hydroxide obtained in the form of a suspension, wet cake, or dried material, is treated with basic silica sol under conditions which exclude the coagulation of a sol. However, these conditions promote the reaction
20 between hydroxylated silica particles of the sol and the hydroxylated surface of titanium hydroxide or titanium dioxide.

In case of using the second type of starting materials in the form of an aqueous suspension, wet cake or dough, it is mixed with an alkali constituent selected from urea, ammonia, sodium or potassium hydroxide,
25 leading a titanium hydroxide or titanium dioxide having a pH in the range of 6.0 to 11.0. To the resulted mixture, a basic silica sol is introduced and a reaction occurs between the hydroxylated surface of silica particles and the hydroxylated surface of titanium hydroxide or titanium dioxide.

The process of the modified titanium dioxide preparation from the first
30 type of starting material consists of the following steps:

- a. preparing the initial sulfate solution;
- b. precipitation of Titanium hydroxide from the above mentioned sulfate solution in the presence of urea followed by a hydrothermal treatment of the formed Titanium hydroxide in its mother liquor, also in the presence
5 of urea as modifier;
- c. separation of the formed precipitated Titanium hydroxide and its washing;
- d. the dough, wet cake, or dried material, or the resulted water suspension of the formed precipitated Titanium hydroxide treatment with
10 basic silica sol as the modifying agent;
- e. filtration of Titanium hydroxide and washing with water; and
- f. transformation of Titanium hydroxide into Titanium dioxide by a heating treatment.

The detailed description of the procedure for obtaining the modified
15 titanium dioxide, using the first type of starting material is as follows:

In stage (a) an aqueous acid solution comprising titanyl sulfate is partially neutralized, thus producing a mixture of sulfate salts having a pH up to + 1.7 and preferably in the range of between 0.02 to 1.2. This neutralization is carried out with various alkali compounds such as
20 sodium hydroxide, sodium carbonate, potassium carbonate or bicarbonate, an aqueous solution of ammonia, calcium compounds, etc. In case of the calcium compounds, an insoluble calcium sulfate is produced and preferably it has to be separated from the neutralized solution. The solution obtained can be used for titanium hydroxide
25 precipitation, following a hydrothermal treatment (stage b) containing a mixture of titanyl sulfate and another dissolved sulfate salt. Generally, the solution has a concentration in the range of between 20 to 250 g/l titanium and preferably between 40-150 g/l (calculated as TiO_2).

The above solution can be used directly in stage "b" in the presence of
30 urea as modifier, or it can be maintained at a temperature in the range of between 20° to 70° C for a period between 0.3 - 300 hours.

The weight ratio between the quantity of urea added to the solution to the quantity of titanium dioxide present in the solution has to be in the range of between 0.3 to 11.0. Titanium dioxide precipitation takes place either during the urea addition, or during heating the solution to about 80° to 100°C. Although the duration of stage "b" is generally in the range of between 0.5 to 5 hours, the precipitation of titanium hydroxide is quicker. The main part of the above mentioned period is required for the hydrothermal treatment of the precipitated titanium hydroxide. The urea introduced into the sulfate solution reacts in the step of precipitation as well as in the process of hydrothermal treatment of the precipitated titanium hydroxide in its mother liquor. The duration of stage "b" depends on the titanyl sulfate content in the solution, the pH of the solution before urea addition, the amount of urea added and the temperature which prevails in the mixture.

The precipitated titanium hydroxide after being subjected to a hydrothermal treatment is separated from the mother liquor and washed (stage "c").

The titanium hydroxide produced after a thermal treatment at a temperature in the range of between 100°-250° C, is characterized by a high surface area, a developed mesopore structure and a decreased sulfur content. In order to improve the above properties and to enhance its thermal stability, it is necessary to use also a second modifier (stage "d"). For this purpose, titanium hydroxide in the form of a dough, wet cake, suspension or dried material, has to possess a pH in the range of 6.0 to 11.0 and preferably between 8 to 10. This adjustment may be carried out with urea, ammonia or their mixture introduced into the above mentioned dough, wet cake or suspension of the titanium hydroxide. Then, this titanium hydroxide is mixed with basic silica sol having a concentration of between 1% to 40% and preferably in the range of between 3% to 20% by weight calculated as SiO₂. The required quantity of silica sol has to be as a weight ratio of SiO₂ to TiO₂, in the range of between 0.01 to 0.30 and preferably between 0.05 to 0.15.

The temperature during this stage of modification may be between the ambient one and the boiling point of the liquid phase. At the above conditions, an intensive chemical interaction of silica sol with titanium hydroxide takes place. The coagulation of silica sol into silica gel is avoided due to the high pH.

As a result of this interaction, and at a ratio between silica sol and titanium hydroxide of 0.1 by weight, substantially all the quantity of SiO_2 present in the solution is consumed by the titanium hydroxide. When said ratio is above 0.13, some of the residual silica sol can be detected in the respective solution.

The result of the above interaction, when the ratio between the sol and titanium hydroxide is calculated on the weight ratio between SiO_2 and TiO_2 of about 0.1, substantially all the SiO_2 from the solution is consumed by the titanium hydroxide. When the above ratio is above 0.13, some residual sol after the reaction can be detected in the solution.

The rate of interaction between the basic sol and hydroxylated surface of titanium hydroxide or titanium dioxide at ambient temperature is low, but increases when the temperature is also increased. It may be assumed that as a result of this interaction, some chemical bonds $\text{Ti} - \text{O} - \text{Si}$ are formed and as a result, a reinforcement in the structure of the network occurred.

The modified titanium hydroxide can be used either in the form of a wet cake, or a suspension in the catalyst manufacture, or can be dried at a temperature between 100°C - 250°C and after that calcined at about 500°C .

The modified titanium hydroxide obtained was analyzed by the following tests for the dry samples as well as for samples calcined at a temperature between 500°C to 900°C :

- determination of the specific surface area, using the so called "1 point method"

- specific surface area and specific adsorption pore volume, as determined

with a Coulter Instrument SA 3100, and

- the respective chemical analyses, carried out using the known tests.

5 The catalytic activity of the titanium dioxide prepared according to the present invention used in the Claus process, was determined in a bench scale pilot plant, after mixing with an inert filler and the resulted dough conveyed through an extrusion, the wet extrudates being dried and calcined. The detailed procedure of this matter is described in our above
10 mentioned copending patent application.

The titanium dioxide was also tested as a carrier of a catalyst used in the oxidation of organic impurities present in air.

The invention will be hereafter illustrated by a number of examples, being understood that these examples are presented only for a better
15 understanding of the process, without imposing any limitation to the invention as covered by the appended Claims.

EXAMPLE 1.

An amount of 2 kg of solid ammonium titanyl sulfate containing about
20 20% of TiO_2 and 27% water of crystallization, was dissolved in 4 l of demineralized water at room temperature during overnight, using a moderate stirring. The non-dissolved portion was separated by filtration. The resulted solution contained 80 g/l titanyl sulfate (calculated as TiO_2) which corresponds to the formula of the respective double salt
25 $(\text{NH}_4)\text{TiO}_2(\text{SO}_4)$ and an amount of ammonium sulfate. An amount of 175 g of urea was added to 500 ml of the solution, at room temperature and the resulted solution was heated and maintained at a temperature in the range of between 97°C - 102°C for about 3 hours. The precipitated Titanium hydroxide was separated from the mother liquor and washed
30 with demineralized water. The resulted wet cake of titanium hydroxide was suspended in a basic silica sol, prepared from a commercial sodium

silicate solution as known in the art, the pH being increased to about 8.5 by treating with an aqueous solution of ammonia.

An amount of about 41 g of the basic sol was mixed with the titanium hydroxide cake, corresponding to a $\text{SiO}_2 : \text{TiO}_2$ weight ratio of about 0.03. The mixture was maintained at about 90°C for 30 minutes under a moderate stirring. The residual quantity of silicon in solution was negligible. The wet cake of titanium hydroxide was converted into titanium dioxide, by drying first at 110°C for about 2 hours and further at about 250°C for half hour. The properties of the product obtained are given in Table 1.

EXAMPLE 2.

The titanium dioxide was prepared as in Example 1, but the amount of the basic silica sol used corresponded to a weight ratio $\text{SiO}_2 : \text{TiO}_2$ to 0.05 (as in Table 1). The data on the specific surface areas of the prepared sample and the respective thermal stability, compared with typical commercial titanium dioxide, are given in Table 1.

EXAMPLES 3 to 5.

The first stage of titanium dioxide preparation, was based on a titanyl sulfate solution, having a composition similar to a commercial titanyl sulfate and sulfuric acid solution, known as "UNITi 992" produced by Kemira Pigments Inc. The solution (A) contained 9.5% by weight TiO_2 and 37% by weight sulfuric acid was prepared as follows:

An amount of 9.8 kg of a commercial titanium dioxide (hydrolysate) UNITi 908, having a loss on ignition of 19.6 by weight (at 1000°C), was dissolved in an amount of 43.8 kg of boiling sulfuric acid having a concentration of 70% by weight). After cooling, an amount of 1 l of this solution was diluted with an equal volume of demineralized water. The resulted solution having a concentration of 123 g/l TiO_2 , was used in the

Examples 3 to 5. The same solution, but with another content of titanium dioxide, was used in Examples 6 to 18.

In Examples 3 to 5, 1 l of acid titanyl sulfate solution, having a concentration of 123 g/l (calculated as TiO_2) was gradually neutralized
5 with 481 grams of an aqueous solution of ammonia, containing about 25% by weight of ammonia. The temperature of the starting solution was 22°C , but during the neutralization it increased to about 55°C - 65°C and maintained at this level with stirring, for about one hour. To the above solution, an amount of 780 ml of demineralized water was added and the
10 resulted solution had a pH of 0.90. To the above mentioned solution, an amount of 409 g of urea was added and then heated to 98°C and maintained at this level for about two and half hours (see Table 2). The precipitated titanium hydroxide was separated from the mother liquor and washed with demineralized water. The resulted wet cake was divided in
15 three portions, used in the Examples 3, 4 and 5. Each wet cake sample was diluted with demineralized water, obtaining a suspension which had a concentration of 10% (calculated as TiO_2).

A basic silica sol was prepared as known in the art, but different cations were used for the sol stabilization; in Example 3: sodium, in Example 4:
20 potassium and in Example 5: ammonium. In each Example, the amount of basic sol used, calculated as % of SiO_2 to TiO_2 was 10% (by weight). The three different basic silica sols were mixed separately with the above mentioned three samples of suspension and the resulted mixtures were heated to about 90°C and maintained at this temperature
25 for about 1 hour. In each case, substantially all the quantities of silica were consumed by the titanium hydroxide. The resulted precipitates were separated from the liquid phase by filtration and converted into titanium dioxides by a thermal treatment at four different temperatures: 110°C , 500°C , 700°C and 900°C .

30 The conditions for the interaction of precipitated titanium hydroxides with basic sols, are described in Table 3 and the values of specific surface

areas are given in Table 4. Each type of basic silica sol (stabilized with sodium, potassium or ammonium) can act as stabilizer, but as can be noticed, with ammonium the stabilizing effect is higher than with sodium or potassium. Accordingly, the further experiments were carried out with
5 basic silica sols stabilized with ammonium.

EXAMPLES 6 to 17.

In these Examples, the same acidic titanyl sulfate solution (solution A) as described in Examples 3 to 5, was used as a starting material but with a
10 different dissolution before neutralization and also with a different extent of neutralization. The concentrations of the solutions before neutralization, were in the range of between 70 to 128 g/l TiO₂. The pH values of the neutralized final diluted solutions were in the range of between 0.02 to 1.67. The final value for each Example as well as the
15 respective conditions of precipitation are given in Table 2.

In the Examples 6 and 6A the neutralized solution was maintained at 50°C for 5 hours and 30 minutes before urea addition; in Example 15 the neutralized solution was maintained at 55°C for 8 hours after urea addition.

20 In Example 17, the acid titanyl sulfate solution was first neutralized with calcium carbonate reaching a pH of 0.09, then the formed calcium sulfate was filtered out. The final neutralization of the solution was carried out with ammonium bicarbonate, reaching a pH of 0.69 as shown Table 2. The conditions of the precipitated titanium hydroxides in the
25 interaction with the basic sols are given in Table 3. As can be noticed, titanium hydroxide was treated with silica sol, both in suspension and also in a wet cake. The concentrations of sols were changed in a wide range from 3% to 20.6% by weight SiO₂.

The properties of the modified titanium hydroxides are given in Tables 4,
30 8, 9, 10, 11, 12, 13, 14 and X-Ray diagrams for samples 6 and UNITi 908. As can be noticed from these Tables and X-Ray diagrams, modified titanium dioxides are characterized by a significant higher thermal and

hydrothermal stability than the known titania and titania/silica mixed oxides.

The sample prepared in Example 12 was investigated with the EDAX method and the data regarding the respective compositions by weight at different points are presented below:

	TiO ₂	SiO ₂	CaO
point 1	87.5	12.3	0.2
10 point 2	87.7	12.3	absent
Bulk	87.8	12.1	0.1

As can be noticed there are slight variations from one point to another, but titanium and silicon are present in each point. No separate phases of TiO₂ or SiO₂ exist. The calcium presence results from an impurity in the sample.

EXAMPLE 18.

In this Example an acidic silica sol was introduced in a titanyl sulfate solution, neutralized with ammonia in an amount corresponding to 10% as SiO₂ calculated on the TiO₂ content in the solution, present as titanyl sulfate. The resulted solution was heated and the precipitation of titanium hydroxide took place in the presence of silica sol. The other conditions for titanium hydroxides precipitation are given in Table 2.

The effect of high thermal stability is also noticed from the attached X-Ray diagrams (Figures 1 and 2) in respect to Example 6 and compared with commercial TiO₂ (UNITi 908). After calcination at 950°C for 1 hour, sample 6 contains only anatase, at the same time commercial titanium dioxide UNITi 908 was converted only partially into rutile (about 60%).

A definite stabilizing effect can be detected also in this case, although it is less than with the same amount (10%) of the basic silica sol added to the titanium hydroxide under the conditions as described above (compare Examples 5 and 18 in the Tables 2 and 4.)

EXAMPLE 19.

In this example, acid and basic silica sols were used and their modifying effects were compared. The criterion of effectiveness was the decrease in the specific surface area of the titanium dioxides as prepared in Examples 13 and 16. In all these experiments corresponding titanium hydroxides were introduced into silica sols having a concentration of 3% calculated as SiO₂. In one experiment it was an acid sol and in another one, it was a basic sol stabilized with an ammonium cation. As can be noticed from Table 5, both the acid and the basic sols increase the stabilizing effect, but the basic sol provides a much higher stabilizing effect.

EXAMPLES 20-22.

In these Examples, the preparation of titanium dioxide with an enhanced thermal and hydrothermal stability according to the present invention was used and compared with a commercial titanium dioxide. In Examples 20 and 21, titanium hydrolysates (S-140 and S-150) as produced by KEMIRA PIGMENT OY (Finland) were used. In Example 22, a hydrolysate (UNITi 908) produced by KEMIRA PIGMENT (U.S.A.) was used. The beneficial effects of the method according to the present invention, are evident from the Tables 6, 7, 8 and 13.

This can be noticed also from the X-Ray diagrams (see Figures 1 and 3) for the sample 22 compared with the commercial titanium dioxide UNITi 908 calcined at 950°C for 1 hour. The modified titanium dioxide contains only initial crystalline anatase phase, once about 60% of the commercial titanium dioxide had been converted into rutile.

EXAMPLE 23.

In this Example it is demonstrated the effectiveness of the modified titanium dioxide as an active component used in the Claus catalyst.

The modified titanium dioxide as obtained in Example 1, was mixed with powdery silica N60 (produced by PPG) and an acid silica sol. The powdery silica was used as an inert filler and the silica sol was used as a binder component. The composition of this mixture, in weight percentage

5 was as follows:

Modified titanium dioxide	24.9%
Powdery silica	64.6%, and
Silica sol (calculated as SiO ₂)	10.5%,

The mixture was granulated into extrudates with a diameter of 3.6 mm,
 10 dried at 110°C for two hours and then calcined at 400°C for three hours.
 The results with this catalyst tested in a bench scale pilot plant, using the known

conditions as used in the Claus process were as follows:

	The reaction	The catalytic activity (%)
15	H ₂ S + SO ₂	100 *
	COS + H ₂ O	100
	CS + H ₂ O	98.

(*expressed the activity as shown by the conversion related to the equilibrium),

20

EXAMPLE 24

This Example shows that the modified titanium dioxide can be used also as a carrier for catalysts which is effective in the oxidation of organic compounds in a gas phase.

25 Two samples were prepared and tested in a laboratory unit for the catalytic oxidation of propane (3 mol.%) in air at 400°C. In the two cases titanium dioxide was doped with vanadium oxide.

The compositions of the catalysts and the results of the respective tests are given in Table 14. As can be noticed the titanium dioxide as
 30 prepared by the present invention, is useful as a catalyst carrier for organic impurities in air oxidation.

EXAMPLE 25.

An experiment was carried out, to show that the titanium dioxide according to the present invention can be successfully used as a photocatalyst for detecting organic impurities in water oxidation. The
5 titanium hydroxide precipitated from a sulfate solution in the presence of urea and after washing was separated in the form of a wet cake containing 25% by weight TiO_2 before the treatment with basic silica sol (as in Example 7).

The procedure of the testing consists in the use of a suspension of 0.15 -
10 0.30 grams, calculated as TiO_2 placed in a bottle of 2 l. A quartz tube (internal diameter 1 cm and length 1 m) was used as a sun radiation reactor. Through this reactor and a bottle of water a stream containing 35 to 44 ppm of atrazine was pumped through.

A comparative test with a commercial titanium dioxide (P 25, as produced
15 by Degussa) was used for photodegradation of organic impurities in water. As can be noticed from Table 16, the titanium dioxide according to the present invention can be useful also as a photocatalyst for this purpose.

20

25

30

TABLE 1:**Specific surface areas of titanium dioxides modified with urea**

5 in the process of titanium hydroxides precipitation from a solution
of ammonium titanyl sulfate, following a hydrothermal treatment
in its mother liquor and then modified with basic silica sol.

10	Example No.	Specific surface area of TiO ₂ modified with urea m ² g ⁻¹	Quantity of introduced silica sol calculated as% SiO ₂ in TiO ₂	Specific surface area of samples treated with basic silica sol, m ² g ⁻¹		
				Dried sample	After calcination for 3 hours at a temperature of, °C	
					500	700
15	1.	392	3	436	207	113
	2.	399	5	448	283	144
	Commercial TiO ₂ UNITi					
20	908	328 ^x			93 ^x	24 ^x

^x UNITi 908 was tested without treatment with basic silica sol.

25

30

TABLE 2:

Conditions of titanium hydroxides precipitation and hydrothermal treatment in the presence of urea.

Example No.	Concentration of TiO ₂ in a solution neutralized with ammonia as g/l	pH of the neutralized solution	Weight ratio urea:TiO ₂	Duration of heating, (hours)	
10	3-5	123	0.90	3.3	2.6
	6 and 6A	125	1.10	3.6	2.5
	7	128	0.80	2.0	2.5
	8-9	128	1.67	2.0	5.5
15	10	123	0.80	2.8	2.3
	11	70	0.97	2.9	3.5 —
	12	123	0.84	3.6	4.0
	13	120	0.97	2.1	3.5
	14	126	0.02	10.3	3.0
20	15	122	0.92	3.6	2.3
	16	126	1.20	1.5	2.5
	17	91	0.69	2.63	2.2
	18	70	0.93	3.0	3.5

25

30

TABLE 3:**5 Conditions of titanium hydroxides interaction with basic silica sols.**

Example No.	Concentration of titanium hydroxide in suspension (as % TiO2)	Concentration of silica sol, (as g/l SiO2)	Cationic form of silica sol	Quantity of silica sol calculated as % SiO2 in TiO2			
				Introduced in suspension or in cake	Taken up by titanium hydroxide		
10	3	10	3.0	Na	10.0	9.9	
	4	10	3.0	K	10.0	9.9	
	5	10	2.9	NH4	10.0	9.9	
	15	6	10	3.2	NH4	7.0	6.9
		6A	10	3.3	NH4	15.0	13.8
7		10	3.0	NH4	2.0	2.0	
8		10	3.4	NH4	3.0	3.0	
9		10	3.4	NH4	7.0	6.0	
20	10	wet cake	3.2	NH4	30.0	15.3	
	11	12	3.3	NH4	10.0	10.7	
	12	wet cake	20.6	NH4	16.5	13.4	
	13	15	11.6	NH4	5.0	5.0	

25

30

35

TABLE 4:**Specific surface areas of modified titanium dioxides.**

5	Example No.	Specific surface area, (m ² g ⁻¹)					
		Modified with urea and dried at 110°C	Modified with urea and basic silica sol				
			Dried at 110°C	calcined for 3 hours at			
				500°C	700°C	800°C	900°C
10	3	416	442			141	65
	4	416	434			139	65
	5	416	453	327	277	164	110
	6	424	470	285	170	116	
	6A	424	478	357	269	203	
15	7	393	393			53	28
	8	390	448		111	72	31
	9	390	450		170	119	56
	10	360		312		228	146
	11	403	429			142	81
20	12	406	430	367	269		
	13	400	435	238	141		
	14	434					
	15	460	490				
	16	416					
25	17	402					
	18	365		234	115		
30	(UNITi 908 Commercial TiO ₂)		328	93	24		

TABLE 5:**Comparison of modificatory effects of acid and basic silica sols.**

5	Example No.	Specific surface area of original TiO ₂ , (m ² g ⁻¹)	Type of silica sol	Quantity of silica sol, as % SiO ₂ in TiO ₂	Specific surface area (m ² g ⁻¹), after calcination for 3 h. at a temperature of	
					500°C	700°C
10	13	400	acidic	8		107
	14	400	basic	5	242	145
	15	416	acidic	4	155	62
	16	416	basic	4	230	123
	17	416	without		111	8

15 **TABLE 6:****Commercial titanium dioxides modified with silica sol.**

20	Example No.	The sample of the TiO ₂ used	Quantity of used TiO ₂ (grams)	Concentration of silica sol as % SiO ₂ in sol	Suspension or wet cake were treated	Quantity of silica sol as % SiO ₂ calculated on TiO ₂	
						introduced in the suspension or in the cake	taken up by TiO ₂
25	20	S-140	200	3.1	suspension	7	
	"	S-140	200	3.1	suspension	10	
	"	S-140	200	3.1	suspension	14	
	21	S-150	200	3.3	suspension	7	
	"	S-150	200	3.3	suspension	10	
	22	UNITi 908	10	20.6	wet cake	15	13

30

TABLE 7:

Specific surface areas of commercial titanium dioxides
modified with ammonium silica sols

Example No.	Quantity of silica sol as % SiO ₂ in TiO ₂	Specific surface area, m ² g ⁻¹				
		Dried sample	Calcined for 3 hours at various temperatures:			
			500°C	700°C	800°C	900°C
20	none	329 ^x		16		
"	7			101	58	
"	10			119		
"	14		191	143	94	
21	7	290	234	102	90	
"	10			126		
22	15		227	210	116	80
"	none	328	93	24		

(^x measured by a Coulter Instrument)

TABLE 8:

Hydrothermal stability of the modified titanium dioxides
in comparison with known ones.

Example No.	Specific surface area (m ² g ⁻¹), after steaming ^x during 5 hours at 400°C
6	173
6 A	320
21	132
Commercial TiO ₂ :	
UNITi 908	94
S-150	84

Note: ^x the steaming stream contained 90% by volume water vapors and 10% by volume air.

TABLE : 9**5 Sulfur content of modified titanium dioxides**

	Example No.	Sulfur content, (% by weight)	
		Calculated as sulfur	Calculated as (SO ₄ ²⁻)
10	1	0.04	0.12
	5	0.24	0.72
	10	0.10	0.30
	22	0.07	0.21
	Commercial		
15	titanium dioxide	0.3-1.0	0.9-3.0

20

25

30

TABLE 10:

**Specific surface area distribution on pore diameters of
modified titanium dioxides in comparison with known ones.**

5	Example	Total specific surface area		Specific surface area formed by pores with a diameter greater than:					
				4.10 nm		3.5nm		3.3nm	
		m ² g ⁻¹	In % of analogous value for a commercial sample S-140	m ² g ⁻¹	In % of analogous value for a commercial sample S-140	m ² g ⁻¹	In % of analogous value for a commercial sample S-140	m ² g ⁻¹	In % of analogous value for a commercial sample S-140
10									
15	<u>Example 6</u> TiO ₂ before treating with basic silica sol.	424	129	180	269	334	380	352	352
20	TiO ₂ treated with basic silica sol as described in Example 6	470	143	251	375	352	400	371	371
25	<u>Example 6A</u> TiO ₂ treated with basic silica sol as described in Example 6A	476	145	319	476	367	417	378	393
30	<u>Example 15</u> TiO ₂ before treating with basic silica sol	490	149	182	272	242	275	259	270
35	Commercial TiO ₂ - UNITi-908	328	100	48	72	62	70	67	70
	Commercial TiO ₂ S-140	329	100	67	100	88	100	96	100

Note: all the data listed in this Table were measured with Coulter Instrument SA 3100.

40

TABLE 11:

The adsorption pore volume distribution on pore diameters of modified titanium dioxides compared with known ones.

5

Example	Adsorption pore volume formed by pores with diameter					
	less than 100 nm		greater than 4.1 nm		greater than 3.5 nm	
	cc/g	In % of analogous value for commercial sample S-140	cc/g	In % of analogous value for commercial sample S-140	cc/g	In % of analogous value for commercial sample S-140
10						
Example 6 TiO ₂ before the treatment with basic silica sol	0.47	147	0.23	110	0.41	178
15						
TiO ₂ treated with basic silica sol as described in Example 6	0.52	163	0.31	148	0.41	178
20						
Example 6 A TiO ₂ treated with basic silica sol as described in Example 6 A	0.63	180	0.49	233	0.64	235
25						
Example 15 TiO ₂ before the treatment with basic silica sol	0.56	160	0.36	171	0.40	174
Commercial TiO ₂ UNITI- 908	0.32	91	0.20	105	0.22	96
30						
Commercial TiO ₂ S-140	0.35	100	0.21	100	0.23	100

Note: all the data listed in this Table were measured with Coulter Instrument SA 3100.

35

40

TABLE 12:

Comparison of thermal stability of the modified titanium dioxide prepared according to the present invention and a mixed titania-silica oxides as described in the US Patent 4,221,768

Samples prepared according to the present invention and calcined at 500°C for 3 hours			Samples as described in the US Patent 4,221,768 (calcined at 500°C for 3 hours)			
10	Example No.	TiO ₂ content of the sample, (% by weight)	Specific surface area (m ² g ⁻¹)	Example	TiO ₂ content of the sample (% by weight)	Specific surface area (m ² g ⁻¹)
	12	86	367	1	84	220
				4	84	280
15	5	90	327	6	91	230

TABLE 13:

20

Specific surface areas of calcined titanium dioxide according to the present invention, compared with those described in the European Patent Applications Nos.: 0576120 and 0311515.

25	Conditions used in calcination		Specific surface area of calcined samples, (m ² g ⁻¹)			
	temperature °C	duration, hours	The present invention		EP 0576120	EP 03115115
			Example 6	Example 10	Example 1	Example Q
	575	1	229	360		93
	575	7	210	350		85
30	800	3	116	228	65.6	

TABLE 14:

Comparison between structural indicators of calcined samples prepared according to the present invention and those described in the literature.

Prepared according to the present invention					Described in literature				
Example	Quantity of silicon introduced in the titania's structure calculated as SiO ₂ , %	Calcining conditions		Specific surface area (m ² g ⁻¹)	Quantity of silica in titania/ mixed oxides (%)	Calcining conditions		Specific surface area (m ² g ⁻¹)	References
		Temperature °C	Duration hours			Temperature °C	Duration hours		
10	5	9.9	700	3	277	20.0	600	85	Applied Catalysis A: General 139(1996) 175-187
	6	6.9	700	3	170				
	8	3.0	700	3	111				
	5	9.9	800	3	164				
20	10	15.3	900	3	146				Journal of catalysis 105,511-520 (1987)
	6	6.9	500	3	285	25.0	500	2	
	6 A	13.8	500	3	357				
	12	14.0	500	3	367				
	21	7.0	500	3	234				
25	22	15.0	500	3	227				

TABLE 15:

Catalytic oxidation of propane in air at 400°C.

	Number of samples from which titanium dioxide was taken	Quantity of vanadia introduced into TiO ₂ (% by weight)	Quantity of doped TiO ₂ in catalyst (% by weight)	Quantity of siliceous filler and binder in catalyst (% by weight)	Extent of oxidation, (%)
35	5	3	Doped titania as was used		100
	12	5	38	62	100

40

TABLE 16:**5 Photodegradation of atrazine in aqueous solutions**

Sample	<u>Duration of degradation, hours</u>			
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>
<u>Concentration of atrazine in ppm</u>				
10 Titanium hydroxide from Example 7	35	28	23	17
P-25 (Degussa)	44	20		17

15

20

25

30

CLAIMS :-

5

1. A novel titanium dioxide modified with urea in the stage of a titanium hydroxide precipitation from an aqueous solution containing a mixture of dissolved sulfate salts, including titanyl sulfate, following by a hydrothermal treatment of the precipitated hydroxide in its mother liquor and then modified with a basic silica sol in the stage of the formed titanium hydroxide or dried titanium dioxide, being characterized by a high catalytic activity, an enhanced thermal stability as measured by a specific surface area of up to $240 \text{ m}^2/\text{g}$ for a sample in which 15% of silicon (calculated as SiO_2) was introduced into the titanium hydroxide structure during the interaction with basic silica sol and calcined at 800°C for three hours.
2. The novel modified titanium dioxide according to Claim 1, possessing a developed mesopore structure, a decreased sulfur content, a high hydrothermal stability as measured by a specific surface area of up to $350 \text{ m}^2/\text{g}$ for the mentioned sample subjected to a hydrothermal treatment for five hours with a water vapor-air mixture containing 90% by volume of water vapor at 400°C .
3. The novel modified titanium dioxide according to Claims 1 and 2, being characterized by a specific surface area of up to $520 \text{ m}^2/\text{g}$.
4. The novel modified titanium dioxide according to Claims 1 to 3, being characterized by a mesopore structure as measured by an adsorption pore volume formed by pores with a diameter less than 100 nm of up to 0.65 cc/g .
5. The novel modified titanium dioxide obtained from a suspension, wet cake or dry hydrolysate of white titanium pigment and modified with a basic silica sol, being characterized by an enhanced thermal stability as

measured by a specific surface area of up to $125 \text{ m}^2/\text{g}$ for a sample in which 15% of silicon (calculated as SiO_2) was introduced into a titanium hydroxide structure during the interaction with basic silica sol and calcined at 800°C for three hours.

- 5 6. The novel modified titanium dioxide according to Claims 1 or 5, containing at least 1% silicon by weight (calculated as SiO_2), introduced into titanium dioxide or titanium hydroxide structure, during the interaction with basic silica sol.
7. The novel modified titanium dioxide according to Claims 1 and 5,
10 containing a minimum sulfur content of 0.02%.
8. A method for obtaining the novel modified titanium dioxide according to Claim 1, using a precipitated titanium hydroxide produced from an aqueous sulfate solution having an initial pH of up to 1.7 and comprising, besides titanyl sulfate, other compounds selected from sodium,
15 potassium, ammonium, calcium and magnesium sulfates.
9. The method for obtaining the novel modified titanium dioxide according to Claim 8, wherein the preferred pH of the above mentioned solution, comprising besides titanyl sulfate at least one of the above sulfates is in the range of between 0.02 to 1.2.
- 20 10. The method for obtaining the novel modified titanium dioxide according to Claim 8, wherein said titanium hydroxide is precipitated from a sulfate solution having a titanium content in the range of between 20 g/l to 150 g/l (calculated as TiO_2).
11. The method for obtaining the novel modified titanium dioxide
25 according to Claim 1, wherein the amount of urea introduced in the sulfate solution is in the range of between 0.3 to 11 as weight ratio urea to titanium dioxide.
12. The method for obtaining the novel modified titanium dioxide according to Claim 8, wherein said sulfate solution is maintained at a
30 temperature in the range of between 0° to 70°C for at least half hour before or after urea introduction in the solution.

13. The method for obtaining the novel modified titanium dioxide according to Claim 8, wherein the titanium hydroxide is precipitated and subjected to a hydrothermal treatment in its mother liquor at a temperature in the range of between 70°C to 200°C for at least half hour.
- 5 14. The method for obtaining the novel modified titanium dioxide according to Claim 8, wherein the aqueous sulfate solution is obtained by dissolution of ammonium titanyl sulfate in water or in a sulfate solution.
15. The method for obtaining the novel modified titanium dioxide according to Claims 5 to 8, wherein the titanium component present in the
10 form of an aqueous suspension, a wet cake, a dough, or dry material, is treated for increasing the pH in the range of between 6.0 to 11, and preferably between 8.0 to 10.0 and then subjected to the modification with a basic silica sol.
16. The method for obtaining the novel modified titanium dioxide
15 according to Claim 15, wherein said pH adjustment is carried out by an alkali constituent, selected from urea, ammonia gaseous or aqueous solution, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, calcium hydroxide or a mixture thereof.
- 20 17. The method for obtaining the novel modified titanium dioxide according to Claims 15 and 16, wherein said modification with basic silica sol is carried out at a temperature below the boiling point of the respective mixture.
18. The method for obtaining the novel modified titanium dioxide
25 according to Claim 17, wherein the basic silica sol has a concentration in the range of between 1% to 40% by weight (calculated as SiO₂) and a pH above 7.0.
19. The method for obtaining the novel modified titanium dioxide according to Claims 15 to 18, wherein the basic silica sol used, is in a
30 weight ratio of SiO₂ to TiO₂ in the range of between 0.01 to 0.30.
20. The novel modified titanium dioxide according to Claim 1, to be used as a catalyst in the Claus reaction, carbonyl sulfide or carbonyl

disulfide. hydrolysis, photocatalytic degradation of organic impurities in water and as a carrier for a catalyst useful in the oxidation of organic impurities present in gaseous streams.

5

10

15

20

25

30

- 33 -

SUBSTITUTE SHEET (RULE 26)

X-Ray diagram for commercial Titanium Dioxide (UNITi908) calcined at 950C for 1hour

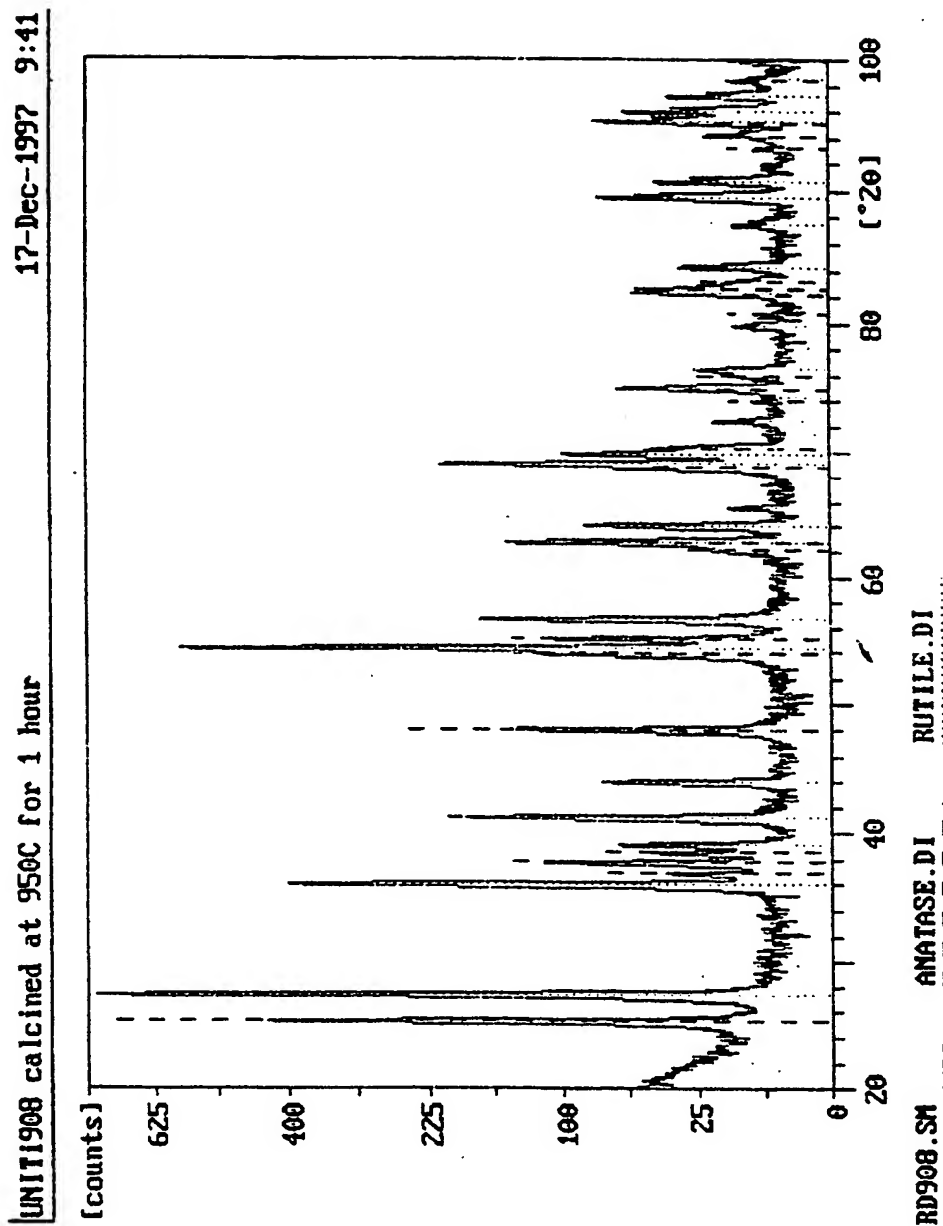
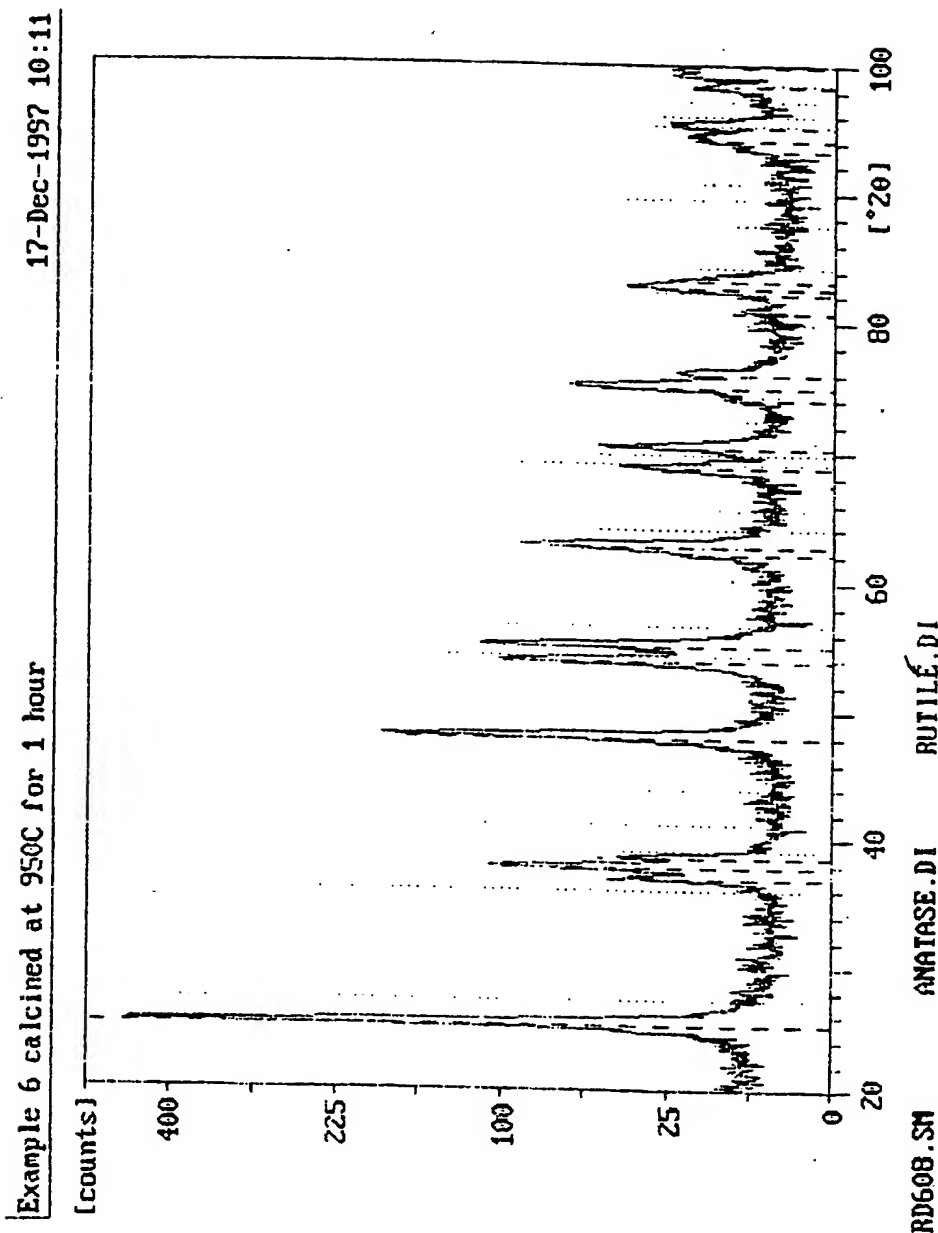


Figure 1

BEST AVAILABLE COPY

SUBSTITUTE SHEET (RULE 26)

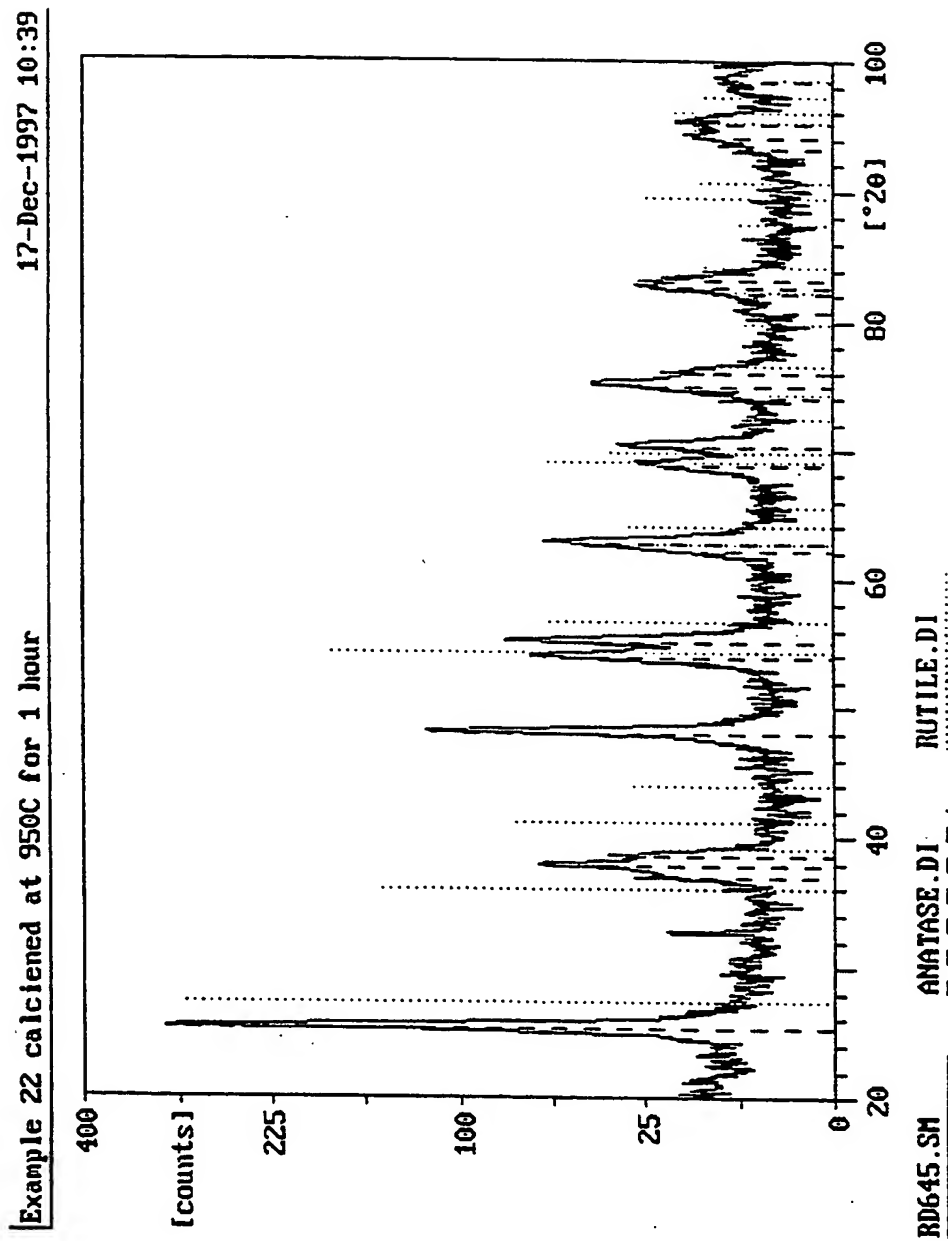
X-Ray diagram for modified Titanium Dioxide(example 6) calcined at 950C for 1 hour



BEST AVAILABLE COPY

Figure 2

X-Ray diagram for modified Titanium Dioxide (example 22) calcined at 950C for 1 hour



BEST AVAILABLE COPY

Figure 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL98/00090**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C01G 23/053; C01B 39/00; B01J 23/00

US CL : 502/349, 350; 423/610, 701, 702, 705, 713; 106/436; 501/134

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,120,701 A (BRAND ET AL.) 09 JUNE 1992, COLUMN 2, LINE 50 - COLUMN 4, LINE 14.	1, 2, 5, 6, 8-14, 18, 20
A	US 4,176,089 A (CULL) 27 NOVEMBER 1979, SEE THE ENTIRE DOCUMENT.	1, 2, 5, 6, 8-14, 18, 20
A	US 4,977,127 A (RIKIMARU ET AL.) 11 DECEMBER 1990, SEE THE ENTIRE DOCUMENT	1, 2, 5, 6, 8-14, 18, 20
Y	US 4,537,873 A (KATO ET AL.) 27 AUGUST 1985, SEE COLUMN 3, LINES 9-20	1, 2, 5, 6, 8-14, 18, 20
Y	US 4,081,510 A (KATO ET AL.) 28 MARCH 1978, SEE COLUMN 4, LINES 34-45.	1, 2, 5, 6, 8-14, 18, 20
Y	US 5,718,878 A (ZHANG) 17 FEBRUARY 1998, COLUMN 2, LINES 26-65.	1, 2, 5, 6, 8-14, 18, 20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 MAY 1998

Date of mailing of the international search report

15 JUN 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ELIZABETH WOOD

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/IL98/00090**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 3, 4, 7, 15-17 AND 19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.